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(54) MANUFACTURE OF FUMED SILICA

(71) We, WACKER-CHEMIE GMBH., a body corporate organised according to the laws of the Federal Republic of Germany, of 8 München 22, Prinzregentenstrasse 22, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for the manufacture of fumed silica by flame hydrolysis.

Highly disperse fumed silica may be manufactured by flame hydrolysis, which comprises burning a gaseous silicon compound and, optionally, another gas that will burn to form water, with oxygen in a flame (*cf.* German Patent Specification No. 900,339). Satisfactory results can be obtained by this method when silicon tetrachloride is used as the gaseous, silicon compound. It is, however, often advantageous to use an organosilane as the gaseous silicon compound but the silica produced from these compounds tends to be contaminated with carbon and thus dark in colour.

The present invention now provides a process for the manufacture of fumed silica, which comprises the steps of:

(i) feeding a liquid organosilane into an evaporation vessel at such a rate that the liquid level within the said vessel remains substantially constant;

(ii) evaporating the liquid organosilane within the said vessel under a pressure within the range of from 0.2 to 1.2 atmospheres gauge and at a temperature of not more than 45°C above the boiling point of the organosilane at 760 torr;

(iii) maintaining the resulting gaseous organosilane at the said temperature until it is

(iv) mixed with a gas comprising at least 15% by volume of oxygen and, optionally, with a gas (other than a gaseous organosilane) that will burn to form water;

(v) feeding the resulting gas mixture into a combustion chamber *via* a conical inlet nosszlet, while

(vi) feeding additional oxygen-containing gas into the combustion chamber *via* an annular nozzle surrounding the conical inlet nozzle;

(vii) combusting the gas mixture within the combustion chamber at a temperature of at least 1100°C, while

(viii) cooling the combustion chamber by means of an indirect positive cooling means.

Fumed silica manufactured according to the process of the invention surprisingly generally has a higher chemical purity than that of fumed silica manufactured from organosilanes in known flame-hydrolysis processes and, in particular, is substantially free of carbon-containing impurities.

The organosilane used in the present process may be one that has been or could be used in a previous flame-hydrolysis process for the manufacture of fumed silica. Tetramethylsilane or a methylchlorosilane, which may be manufactured by reacting silicon or a silicon alloy with methyl chloride, is preferably used as the organosilane. Examples of suitable methylchlorosilanes are methyltrichlorosilane, methyldichlorosilane, dimethyldichlorosilane, trimethylchlorosilane and *sym*-dimethyldichlorodisilane. Methyltrichlorosilane is particularly preferred because it is readily available. A mixture of two or more organosilanes may be used.

The liquid organosilane is fed into an evaporation vessel at such a rate that the liquid level within the vessel remains substantially constant, for which purpose the feed rate of the liquid organosilane should, of course, be the same as the evaporation rate (expressed in weight per unit time). The organosilane is evaporated within the said vessel under a pressure within the range of from 0.2 to 1.2 atmospheres gauge, preferably from 0.4 to 0.9 atmospheres gauge, and at a temperature of not more than 45°C above the boiling point of the organosilane

at 760 torr, preferably at a temperature within the range of from 20 to 35°C above the said boiling point. Heating of the heated surface within the evaporation vessel may be effected, for example, by means of hot water at a temperature within the range of from 95 to 100°C or water vapour under a pressure of up to 1.5 atmospheres gauge.

The gaseous organosilane is subsequently mixed with an oxygen-containing gas and, optionally, with a gas (other than a gaseous organosilane) that will burn to form water. Until this mixing occurs, however, the temperature of the gaseous organosilane must be maintained at the evaporation temperature in order to prevent any condensation of the organosilane. This may be achieved for example, by protecting the pipe through which the organosilane passes from the evaporation vessel to the point at which mixing occurs against heat-radiation by means of a heat-insulating material and/or by providing the said pipe with a heating jacket through which hot water at a temperature within the range of from 95 to 100°C or water vapour under a pressure of up to 1.5 atmospheres gauge is passed.

The additional water-forming gas may be any such gas that could be used in previous flame-hydrolysis processes for the manufacture of fumed silica from a gaseous silicon compound. Examples of such gases are hydrogen, water gas, town gas (coal gas), methane, propane and gaseous methanol. The amount, if any, of this additional gas should be sufficient to ensure complete hydrolysis of the organosilane, for example complete hydrolysis of all silicon-chlorine bonds in the organosilane, and should also be sufficient that a temperature of at least 1100°C is achieved in the reaction flame. The amount of this additional gas is advantageously such that the molar ratio of the organosilane to this additional gas is within the range of from 1:0 to 1:12, preferably from 1:3 to 1:4.5.

The oxygen-containing gas comprises at least 15% by volume of oxygen. It may consist of pure oxygen or of a mixture of oxygen and an inert gas, for example nitrogen. The oxygen-containing gas may be used in the amount mentioned in German Patent Specification No. 900,339, that is advantageously in excess of at least 5% by weight, preferably an excess of from 10 to 50% by weight, based on the stoichiometric amount of oxygen relative to all oxidisable compounds and/or groups present.

The mixing of the gaseous organosilane with the oxygen-containing gas and, optionally, the additional water-forming gas advantageously occurs immediately upstream of the conical inlet nozzle through which the gas mixture enters the combustion chamber. This conical inlet nozzle is surrounded by an annular nozzle (a flushing nozzle), which advantageously has a width within the range of from 0.2 to 2 mm, through which additional oxygen-containing gas is introduced into the combustion chamber. The amount of oxygen-containing gas introduced through the annular nozzle is advantageously an additional excess of from 5 to 15% by weight, preferably about 10% by weight, based on the stoichiometric amount of oxygen as defined above.

A suitable nozzle arrangement is shown, by way of example only, in the accompanying drawings in which

Fig. 1 shows a longitudinal cross-sectional view of the nozzle arrangement, on the line I—I of Fig. 2, and

Fig. 2 shows a plan view of the nozzle arrangement, in the direction shown by the arrow II in Fig. 1.

The gas mixture comprising, for example, methyltrichlorosilane, air and hydrogen is passed through the pipe 10 into the conical nozzle 11, which has an opening 12 having an internal diameter of 50 mm. Additional air is passed through three tangential pipes 13, 13[1], 13[11] and thus fed to an annular nozzle 14 surrounding the conical nozzle 11 and having a width of 0.5 mm.

The gas mixture is burnt in the combustion chamber, thus producing a large amount of heat, which is conducted away by means of an indirect positive cooling means. This may be achieved by cooling the walls of the combustion chamber with air or by providing the combustion chamber with a jacket for a liquid coolant.

Fumed silica manufactured according to the present process is generally in the form of highly disperse silica having an average particle size of less than 1 μm and a BET specific surface area of from 150 to 400 m^2/g. (The term "BET specific surface area" means the specific surface area as determined by nitrogen adsorption according to the method given in ASTM Special Technical Publication No. 51 (1941) pages 95—105, which is usually known as "the BET method".) It is very suitable for use in thickening both polar and non-polar liquids and also as a reinforcing filler in organopolysiloxane compositions curable to elastomers, which compositions may, for example, be heat-vulcanisable compositions containing peroxidic cross-linking agents, one-component or two-component room-temperature-vulcanisable compositions, or compositions in which crosslinking is achieved by adding silicon-bonded hydrogen to aliphatic multiple bonds.

The following examples illustrate the process of the invention. (The symbol "Nm^3" means a "normal cubic metre", that is a cubic metre measured at standard temperature and pressure.)

Example 1

Liquid methyltrichlorosilane was fed into an evaporator at a rate of 28 kg/h under a pressure of 1.5 atmospheres gauge by means of a diaphragm piston pump. The evaporator had a heat-radiating surface which had a surface area of 0.5 m^2 and was heated by means of water vapour under a pressure of 0.5 atmospheres gauge. The flow of the water vapour was controlled by means of a "Samson" (Trade Mark) regulator, which itself was controlled by the vapour pressure of the methyltrichlorosilane in the evaporator in such a manner that the said vapour pressure was maintained at 0.5 atmospheres gauge and that the liquid level of the methyltrichlorosilane was held constant. The temperature in the evaporator was about 78°C.

The gaseous methyltrichlorosilane was passed from the evaporator to a burner nozzle *via* a pipe provided with a jacket through which water vapour flowed under a pressure of 0.5 atmospheres gauge and also provided with a regulating device to maintain a constant temperature.

Immediately upstream of the burner nozzle the gaseous methyltrichlorosilane (28 kg/h) was mixed with 15 Nm^3/h of hydrogen and 105 Nm^3/h of air. The resulting gas mixture was fed through the conical nozzle 11 of the nozzle arrangement shown in the drawings while 8 Nm^3/h of air was fed through the annular nozzle 14.

The gas mixture issuing from the nozzle arrangement was burnt in a combustion chamber having a length of 350 cm and a diameter of 60 cm and surrounded by a 5 cm-wide jacket through which air at 20°C was sucked at a rate of 800 Nm^3/h.

Highly transparent fumed silica was obtained, which had an average particle size of less than 1 μm and a BET specific surface area of 207 m^2/g.

Example 2

The procedure of Example 1 was repeated with the variations that the 28 kg/h of gaseous methyltrichlorosilane was mixed with 1.2 Nm^3/h of propane and 125 Nm^3/h of air (instead of with 15 Nm^3/h of hydrogen and 105 Nm^3/h of air) and that the conical nozzle used had an internal diameter of 70 mm (instead of 50 mm).

Fumed silica having an average particle size of less than 1 μm and a BET specific surface area of 196m^2/g was obtained.

Examples 3

The procedure of Example 2 was repeated with the variation that 30 kg/h of dimethyldichlorosilane were used (instead of 28 kg/h of methyltrichlorosilane).

Fumed silica having an average particle size of less than 1 μm and a BET specific surface area of 189 m^2/g was obtained.

Example 4

The procedure of Example 2 was repeated with the variations that a mixture of 15.5 kg/h of methyltrichlorosilane and 10 kg/h of tetramethylsilane was used (instead of 28 kg/h of methyltrichlorosilane) and that 140 Nm^3/h of air was mixed therewith (instead of 125 Nm^3/h).

Fumed silica having an average particle size of less than 1 μm and a BET specific surface area of 123 m^2/g was obtained.

WHAT WE CLAIM IS:—

1. A process for the manufacture of fumed silica, which comprises the steps of:

(i) feeding a liquid organosilane into an evaporation vessel at such a rate that the liquid level within the said vessel remains substantially constant;

(ii) evaporating the liquid organosilane within the said vessel under a pressure within the range of from 0.2 to 1.2 atmospheres gauge and at a temperature of not more than 45°C above the boiling point of the organosilane at 760 torr;

(iii) maintaining the resulting gaseous organosilane at the said temperature until it is

(iv) mixed with a gas comprising at least 15% by volume of oxygen and, optionally, with a gas (other than a gaseous organosilane) that will burn to form water;

(v) feeding the resulting gas mixture into a combustion chamber *via* a conical inlet nozzle) while

(vi) feeding additional oxygen-containing gas into the combustion chamber via an annular nozzle surrounding the conical inlet nozzle;

(vii) combusting the gas mixture within the combustion chamber at a temperature of at least 1100°C, while

(viii) cooling the combustion chamber by means of an indirect positive cooling means.

2. A process as claimed in claim 1, wherein the organosilane is a methylchlorosilane.

3. A process as claimed in claim 1, wherein the organosilane is tetramethylsilane or methyltrichlorosilane.

4. A process as claimed in any one of claims 1 to 3, wherein the liquid organosilane is evaporated under pressure within the range of from 0.4 to 0.9 atmospheres gauge.

5. A process as claimed in any one of claims 1 to 4, wherein the liquid organosilane is evaporated at a temperature within the range of from 20 to 35°C above the boiling point of the organosilane at 760 torr.

6. A process as claimed in any one of claims 1 to 5, wherein the oxygen-containing gas is air.

7. A process as claimed in any one of claims 1 to 6, wherein the additional gas that will burn to form water comprises hydrogen, water gas, town gas, methane, propane or methanol.

8. A process as claimed in any one of claims 1 to 7, wherein the additional gas that will burn to form water is used in an amount of up to 12 moles per mole of the organosilane.

9. A process as claimed in claim 8, wherein the said additional gas is used in an amount within the range of from 3 to 4.5 moles per mole of the organosilane.

10. A process as claimed in any one of claims 1 to 9, wherein the oxygen-containing gas is initially mixed with the organosilane in an amount constituting an excess of at least 5% by weight, based on the stoichiometric amount of oxygen relative to all oxidisable compounds and/or groups present.

11. A process as claimed in claim 10, wherein the oxygen-containing gas is initially mixed with the organosilane in an amount constituting an excess of from 10 to 50% by weight, based on the stoichiometric amount of oxygen relative to all oxidisable compounds and/or groups present.

12. A process as claimed in claim 10 or claim 11, wherein the additional amount of the oxygen-containing gas fed through the annular nozzle is an amount constituting an additional excess of from 5 to 15% by weight, based on the stoichiometric amount of oxygen relative to all oxidisable compounds and/or groups present.

13. A process as claimed in any one of claims 1 to 12, wherein the annular nozzle has a width within the range of from 0.2 to 2 mm.

14. A process as claimed in claim 1, carried out substantially as described in any one of the examples herein.

15. Fumed silica manufactured by a process as claimed in any one of claims 1 to 14.

16. Fumed silica as claimed in claim 15, having an average particle size of less than 1 μm.

17. Fumed silica as claimed in claim 15 or claim 16, having a BET specific surface area (as hereinbefore defined) within the range of from 150 to 400 m^2/g.

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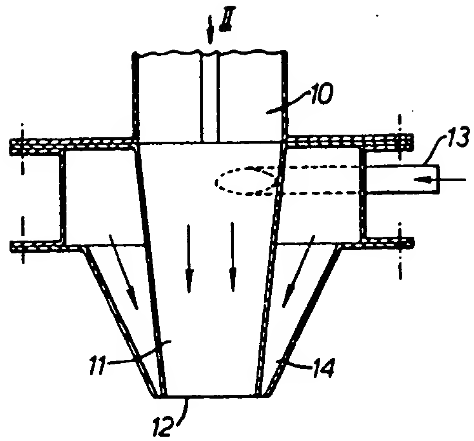

FIG. 1.

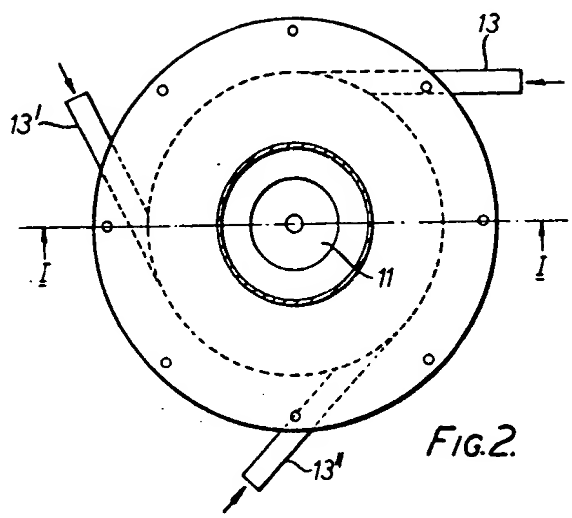

FIG. 2.